PB-226 376

TERMINAL REPORT TO DEPARTMENT OF HEALTH EDUCATION, AND WELFARE, PUBLIC HEALTH SERVICE, NATIONAL AIR POLLUTION CONTROL ADMINSTRATION ON CATALYTIC MECHANISMS FOR NITROGEN OXIDES REDUCTION

Max S. Peters

Colorado University
Boulder, Colorado

1 March 1971

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

009140

PB 226 376

Engineering Research Center
University of Colorado

TERMINAL REPORT TO DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE PUBLIC HEALTH SERVICE NATIONAL AIR POLLUTION CONTROL ADMINISTRATION

on

Research Grant CRG/NAPCA No. AP 00388

"CATALYTIC MECHANISMS FOR NITROGEN OXIDES REDUCTION"

By

Max S. Peters - Principal Investigator
Dean of Engineering and
Professor of Chemical Engineering
University of Colorado
Boulder, Colorado

Boulder, Colorado
March 1, 1971

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

UNIVERSITY OF COLORADO
COLLEGE OF ENGINEERING

March 1, 1971

Mr. Robert V. Paul
Chief, Grants Operation Section
Office of Research Grants
National Air Pollution Control Administration
P.O. Box 12055
Research Triangle Park, North Carolina 27709

Re: ORG/NAPCA
AP 00388

Dear Mr. Paul:

Attached is the final Terminal Report on research grant ORG/NAPCA AP 00388. This work on "Catalytic Mechanisms for Nitrogen Oxides Reduction" was initiated on January 1, 1965, with active work being continued until February 28, 1971, and will be terminated with this final report. The results obtained in this research investigation are summarized in the attached report.

I wish to express my sincere appreciation for the Public Health Service - NAPCA support of this research study. It has enabled us to carry out a research program which we feel has made valuable contributions in the proposed area of scientific and engineering knowledge.

Very truly yours,

Max S. Peters

Max S. Peters
Professor of Chemical Engineering
and
Dean of College of Engineering

MSP:ag

cc: Dr. K. D. Timmerhaus
Mr. H. D. Roark
Dr. R. C. Johnson

Engineering Research Center
University of Colorado

TERMINAL REPORT TO
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL AIR POLLUTION CONTROL ADMINISTRATION

on

Research Grant ORG/NAPCA No. AP 00388

"CATALYTIC MECHANISMS FOR NITROGEN OXIDES REDUCTION"

Prepared by: Max S. Peters

Max S. Peters - Principal Investigator
Dean of Engineering and
Professor of Chemical Engineering
University of Colorado
Boulder, Colorado

Approved by: K. D. Timmerhaus

K. D. Timmerhaus, Director
Engineering Research Center
University of Colorado

Howard D. Roark, Oper. Manager
Research Services Office
University of Colorado

Boulder, Colorado
March 1, 1971

LIST OF CONTENTS

		PAGE
I.	Introduction	1
II.	Summary Statement of Progress toward Original Aims	1
III.	Results of the Research	2
	A. Kinetic Studies of the N_2O-CO Reaction Catalyzed by Chromium-Promoted Iron Oxide	3
	B. Kinetic Studies on the Catalytic Gas Phase Dehydration of Tertiary Butyl Alcohol over Pyrolyzed Polyacrylonitrile	6
	C. Highly Conjugated Organic Polymers as Catalysts for the Dehydration of Tertiary Butyl Alcohol and the Decomposition of Nitrous Oxide	7
	D. Kinetic Studies of the Nitrous Oxide Decomposition Reaction Catalyzed by Nickel Oxide	8
	E. Electron Transport and Solid-State Characteristics of Catalysts	9
	F. Decomposition of Nitrous Oxide Catalyzed by Nickel Oxide	10
	G. Pyrolyzed Polyacrylonitrile as a Catalyst for the Nitric Oxide Reaction	11
	H. Measurement of the Electrical Conductivity of Pyrolyzed Polyacrylonitrile	12
IV.	Personnel	13
V.	Publications	13
VI.	Technical Talks	14

Terminal Report to Department of Health, Education, and Welfare -
Public Health Service - National Air Pollution Control Administration

Research Grant ORG/NAPCA No. AP 00388

CATALYTIC MECHANISMS FOR NITROGEN OXIDES REDUCTION

Reported by Max S. Peters, Principal Investigator
Work done in Department of Chemical Engineering
University of Colorado
Boulder, Colorado

I. Introduction

By copy of letter dated November 25, 1964, research grant AP 00388 was established from the Department of Health, Education, and Welfare - Public Health Service - Division of Air Pollution. The period of the grant was indicated as January 1, 1965, through December 31, 1969, in amounts of $25,590 for the first two years and $25,900 for the last three years. The actual amounts were adjusted each year on the basis of unspent funds and specific requests. The termination date on the grant was extended to February 28, 1971, without additional funds. The grant was to support research on catalytic mechanisms for nitrogen oxides reduction under the direction of Max S. Peters. The research projects conducted under this grant have now been completed, and the results of the research accomplished are summarized in this report.

II. Summary Statement of Progress toward Original Aims

The originally stated aims for this research were to extend the theoretical understanding of catalytic mechanisms involved in nitrogen oxides reduction reactions and to study catalytic activity based on electronic chemical potential. The first aim relative to extending theoretical understanding of catalytic mechanisms for nitrogen oxides reduction has been achieved, in particular as related to the use of inorganic semiconductors as catalysts. Experimental studies have been conducted on the reduction of nitrous oxide and nitric oxide with carbon monoxide using various types of inorganic and organic semiconductors as catalysts for the reduction reactions. The catalytic properties of a large number of materials were determined with particular emphasis being placed on pyrolyzed polyacrylonitrile, nickel oxide, and chromium-promoted iron oxide. Mechanisms for the catalytic reduction reactions were examined and kinetic rate data were obtained.

The electronic chemical potential of both inorganic and organic semiconductors for catalytic activity was examined experimentally. The work was concentrated primarily on the role of pyrolyzed polyacrylonitrile as an organic semiconducting catalyst with studies being made of conductivity characteristics and catalytic activity based on various pyrolysis conditions. The long-term aim of the research, to examine theoretically and experimentally the mechanism of catalytic activity on the basis of solid-state characteristics of semiconductors, has been partially achieved, but much more experimental work is still needed before this ultimate aim is completed.

The research has resulted in improved understanding of the catalytic mechanism of nitrogen oxides reduction, as well as the development of effective catalysts for reduction of nitric oxide. The specific mechanism and kinetic data obtained could be applied for consideration of a catalytic-type muffler for ridding automobile exhaust of nitric oxide.

III. Results of the Research

Research projects completed under the contract include the following:

(A) Kinetic studies of the N_2O-CO reaction catalyzed by chromium-promoted iron oxide, Ph.D. study by Charles A. Leech, III, 1970.

(B) Kinetic studies on the catalytic gas phase dehydration of tertiary butyl alcohol over pyrolyzed polyacrylonitrile, Ph.D. study by Michael B. Cutlip, 1968.

(C) Highly conjugated organic polymers as catalysts for the dehydration of tertiary butyl alcohol and the decomposition of nitrous oxide, M.S. study by Thomas C. Gilman, 1968.

(D) Kinetic studies of the nitrous oxide decomposition reaction catalyzed by nickel oxide, M.S. study by Charles A. Leech, III, 1968.

(E) Electron transport and solid-state characteristics of catalysts, M.S. study by David Y. Yuen, 1966.

(F) Decomposition of nitrous oxide catalyzed by nickel oxide, M.S. study by Eugene G. Sterbis, 1966.

(G) Pyrolyzed polyacrylonitrile as a catalyst for the nitric oxide reaction, David Retzloff, 1969.

(H) Measurement of the electrical conductivity of pyrolyzed polyacrylonitrile, John Shen, 1968.

All of the above-mentioned projects were carried out in the Department of Chemical Engineering at the University of Colorado, and the persons involved were graduate students or post-doctorates in chemical engineering at the University of Colorado. Post-doctorate David Retzloff conducted a study of the characteristics of pyrolyzed polyacrylonitrile and the role of activated carbon for the decomposition of nitrogen oxides. Post-doctorate John Shen, with the support of senior chemical engineering student Wayne Vanderpool, conducted a study on the conductivity characteristics of pyrolyzed polyacrylonitrile. Chemical engineering graduate student Lynn H. Rice conducted a literature survey on pollution abatement reactions with special emphasis on rare metal and rare earth catalysts. Chemical engineering graduate student John Sanderson made a literature survey of inorganic catalysts for reduction of nitric oxide and nitrogen dioxide.

A. Kinetic Studies of the N_2O-CO Reaction Catalyzed by Chromium-Promoted Iron Oxide

An experimental study of the catalytic reduction of nitric oxide and nitrous oxide was conducted using a large number of catalysts. The most effective of the catalysts tested, a chromium-promoted iron oxide catalyst, was then used for further detailed studies of the mechanism of the nitrous oxide reduction by carbon monoxide.

Automotive exhaust gases, one of the major sources of NO_x, contain reducing agents, including CO in relatively large concentrations, that may be capable of reducing NO in a catalytic-type muffler. The reduction of NO to N_2 by CO appears to proceed by the two-step process

$$2NO + CO \rightarrow CO_2 + N_2O$$

$$N_2O + CO \rightarrow CO_2 + N_2.$$

It therefore appears that any catalytic process attempting to reduce NO to N_2 would simultaneously be involved with reducing N_2O to N_2.

The purpose of this work was to investigate prospective catalysts for the NO-CO reaction and subsequently use one of the more promising catalysts in a study of the kinetics of the N_2O-CO reaction. A flow reactor, operated at 250°C, was used in studying the activity of each of the 35 catalysts of

interest. The standard reactant gas (1000 cm^3/min of 10% CO, 5% NO and 85% He) was passed over about 5 grams of each material used. All catalysts were commercially available with the exception of a laboratory-developed pyrolyzed polyacrylonitrile catalyst.

Several catalysts were identified as being quite active in promoting the NO-CO reaction. Cupric oxide-containing catalysts were found to be the most active; however, the cupric oxide is readily reduced by the carbon monoxide, resulting in severe catalyst deactivation. Other active catalysts included a chromium-promoted iron oxide catalyst, cobalt and indium oxides, and supported rhodium, nickel, palladium, and ruthenium.

The chromium-promoted iron oxide catalyst (G-3B Catalyst: Girdler Catalysts Department, Chemetron Chemicals) was selected as the catalyst to be used in the reaction kinetics study. Commercially, this catalyst is used to promote the water-gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$). The sulfur resistant property, the resistance to reduction, and the ability of this catalyst to produce simultaneously the strong reducing agent hydrogen via the water-gas shift reaction, would make this catalyst an attractive one to consider in a catalytic-type muffler designed to rid automotive exhaust of NO and CO.

The reactor used in the kinetics study was operated as a differential reactor in obtaining rate data as a function of temperature and N_2O, CO, N_2, and CO_2 partial pressures. The reactor was operated at 269.9, 253.0, 242.0, and 227.8°C. The only reaction products were N_2 and CO_2. The slow 0-1.75%/hr catalytic deactivation was considered to be the result of a slow reduction of the Fe_2O_3, which is considered to provide the principal catalytic function. The rate data appear to be accurate to within ±5%.

Several reaction rate expressions were examined in the case of isothermal data; however, only an empirical power model and a "modified Freundlich" model were found to fit the data well. The isothermal power model is

$$\text{rate} = A_1 P_{N_2}^{A_2} P_{CO_2}^{A_3} P_{N_2O}^{A_4} P_{CO}^{A_5}$$

and the isothermal "modified Freundlich" model is

$$\text{rate} = B_1 P_{CO}^{B_2} \left(\frac{P_{N_2O}^{2B_3}}{P_{N_2O}^{B_3} + B_4 P_{CO_2}^{B_5}} \right)$$

where A_i and B_i represent constants and P_i represents the partial pressure of the component indicated.

The second model given in the preceding was found to best represent the kinetics of the reaction in light of findings reported in the literature and on the basis of statistical F-tests applied to the various models considered. The "modified Freundlich" model is derived on the basis of a surface reaction between CO, adsorbed on one type of adsorption site adsorbing only CO according to a Freundlich isotherm, and N_2O, adsorbed on a different type of adsorption site adsorbing both N_2O and CO_2 according to a "modified Freundlich" type adsorption isotherm. This model demonstrated that the N_2O-CO reaction has a greater dependency on CO partial pressure than on N_2O partial pressure and that there is a significant retarding effect due to CO_2. No allowance was made for nitrogen adsorption retardation.

Nonisothermal analyses were also made for the two models mentioned. For the nonisothermal power model, $A_1 = k_A^{\circ} e^{-E_{A/RT}}$, while for the more complex nonisothermal "modified Freundlich" model,

$$B_1 = k_B^{\circ} e^{-E_{B/RT}} \left(K_{o_{CO}} \right)^{RT/q_{m_{CO}}} \left(K_{o_{N_2O}} \right)^{RT/q_{m_{N_2O}}}$$

$$B_2 = RT/q_{m_{CO}}$$

$$B_3 = RT/q_{m_{N_2O}}$$

$$B_4 = \left(K_{o_{CO_2}} \right)^{RT/q_{m_{CO_2}}} \left(K_{o_{N_2O}} \right)^{RT/q_{m_{N_2O}}}$$

$$B_5 = RT/q_{m_{CO_2}}$$

where k° = frequency factor for reaction

E = activation energy

R = gas-law constant

T = absolute temperature

K_{o_i} = Freundlich adsorption constant for component indicated

q_{m_i} = mean heat of adsorption for component indicated.

The mechanism of the reaction definitely does not appear to be the alternate oxidation and reduction of the catalyst surface or the decomposition of nitrous oxide to give nitrogen and adsorbed oxygen atoms followed by carbon monoxide reacting with the adsorbed oxygen atoms. Adsorption or desorption of one of the reactants or products does not appear to be the rate-limiting step in the overall mechanism.

B. Kinetic Studies on the Catalytic Gas Phase Dehydration of Tertiary Butyl Alcohol over Pyrolyzed Polyacrylonitrile

The catalytic activity of pyrolyzed polyacrylonitrile, a semiconductive organic polymer, was studied by dehydrating tertiary butyl alcohol to isobutylene and water. The purpose of the study was to obtain some understanding of the catalytic activity of an organic semiconductor and to examine the possibility of interpreting the reaction mechanism on the basis of the electronic theory of catalysis. The study was carried out in a differential reactor at atmospheric pressure and temperatures of 240, 260, and 280°C. Under these conditions, the homogeneous reaction was negligible and dehydration was the only reaction observed. The effect of the partial pressures of alcohol, isobutylene, water, and diluent nitrogen on the reaction rate was evaluated. Analyses of both inlet and outlet reactor streams were made with a gas chromatograph equipped with a heated gas sampling valve.

The catalyst was prepared by heating polyacrylonitrile slowly in air to 230°C, and then in nitrogen to 325°C. Elemental and infrared analyses of the resulting polymer suggested that it was composed of condensed pyridine rings. The surface area of the catalyst as determined by nitrogen adsorption was 17.7 square meters per gram. Pore size distribution measurements were carried out using a combination of nitrogen adsorption and mercury porosimetry.

Various catalytic reaction mechanisms based on electron transport and also on Bronsted surface acidity were evaluated. The electronic mechanisms were examined qualitatively while various Hougen and Watson type rate equations derived from the Bronsted acid mechanism were examined by using nonlinear estimation. This treatment showed that the adsorption of water and isobutylene reduced the reaction rate and must be considered in any mechanism. The experimental data showed that both single and dual site reaction models described the results extremely well. Extension of the results to get independent adsorption data under reaction conditions together with kinetic rate measurements and direct measurements of the electrical properties of the catalyst during the adsorption and reaction rate studies would be necessary to determine for certain if the reaction mechanism involves electron transfer.

C. Highly Conjugated Organic Polymers as Catalysts for the Dehydration of Tertiary Butyl Alcohol and the Decomposition of Nitrous Oxide

The dehydration of tertiary butyl alcohol to isobutylene and water and the decomposition of nitrous oxide to nitrogen and oxygen were studied on the following polymers: pyrolyzed polyacrylonitrile, poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, the benzimidazolimide copolymer of 3,3'-diaminobenzidine and pyromellitic dianhydride, and the polyacene quinone radical polymer from pyromellitic dianhydride and chrysene. Activated oak charcoal and nickel oxide were also used for reference activities. The objectives of this work were to determine whether or not these polymers exhibited any catalytic activity for these reactions and to attempt to correlate the polymer properties related to such activity.

The polymers were prepared either by free-radical solution polymerization or by high-temperature melt polycondensation. The theoretical structures were evaluated by means of elemental analysis and infrared spectroscopy. The dehydration and decomposition reactions were studied in a fixed-bed, tubular, differential reactor. Pure reactant gaseous feeds at 0.8 atmosphere were used. The alcohol reaction was carried out at 240, 260, and 280°C, while the nitrous oxide reaction was followed at 285, 305, and 325°C. The reaction products were analyzed by gas chromatography using a thermal conductivity cell.

It was found that the ranking of polymer activity based on surface area was reversed between the two reactions. It was proposed that this phenomenon might be due to the relative p-type or n-type properties of the polymers because the proposed mechanisms of the reactions would have opposite functionalities for this property. Although the activated charcoal was more reactive on a weight basis, it was found to be less reactive than the majority of the polymers on a surface area basis. The catalytic nature of the polymers for the nitrous oxide reaction was questioned since oxygen was not liberated in stoichiometric quantities.

D. Kinetic Studies of the Nitrous Oxide Decomposition Reaction Catalyzed by Nickel Oxide

An experimental study of the kinetics of the nitrous oxide decomposition was conducted using nickel oxide as the catalyst. The results were interpreted in light of Langmuir-Hinshelwood type mechanisms and were also statistically correlated in a power-law type expression and in a mechanism derived from the charge-transfer theory of gas-surface interactions.

The experimental data were obtained in a tubular, fixed-bed, flow reactor operated as a differential reactor. The reactor was operated at atmospheric pressure at three different temperatures; 293.4°C, 313.3°C, and 333.6°C. The inlet nitrous oxide was diluted with helium, nitrogen, and oxygen, and with combinations of these gases in order to determine their effect as diluents. Conversions ranged from 0.86 to 4.23% of the inlet nitrous oxide. All gas streams were analyzed by a gas chromatograph using a thermal conductivity cell as a detector and employing a "column switching" technique. Under the conditions employed in the reaction, the homogeneous reaction was negligible as was the reverse reaction. No other side reactions were observed.

The best correlation of the rate data was given by the simple power model suggested by Weller and Boudart. The normal sum of squares of the power model was such that, upon applying a statistical F-test, four other models had to be retained. The next best fit to the data was obtained by using a rate expression based on charge transfer theory of the type proposed by V. J. Lee (Ph.D. thesis in Chemical Engineering, University of Michigan, 1963), with a recommended exponent on the nitrous oxide partial

pressure of 2/3. In consideration of the Langmuir-Hinshelwood type rate expressions, a statistically "best" mechanism could not be determined from the data that were obtained. A dual site and a single site model, both derived assuming surface reaction as the rate limiting step, described the data equally well. An activation energy for the reaction of about 33.30 kcal/mole was obtained for the dual site model and a value of about 34.97 kcal/mole was obtained for the single site model. The last model which had to be retained on a statistical basis was eliminated by information reported in the literature which suggested the adsorption of atomic oxygen rather than molecular oxygen on the catalyst surface.

E. Electron Transport and Solid-State Characteristics of Catalysts

This work presented a summary of the present development of organic and inorganic semiconductors as catalysts. An equation that relates partial pressures for N_2O decomposition reaction with solid-state properties of catalysts was proposed.

The basic principle of the electron transport theory of catalysis is that there is an exchange of electrons between the adsorbed particles and the semiconductor catalyst. A rate-limiting step can be one of the following:

1) Formation of adions.
2) Surface migration and reaction of adions.
3) Return of excess charge from adion to catalyst.

The N_2O decomposition reaction was used as an illustration to find the type of semiconductor catalyst to be used for best product yield. The type of semiconductor to be used can be determined from the proposed mechanism of the particular reaction and the type of change of conductivity of the catalyst. The conductivity of a catalyst changes during reaction, and it is assumed that, for N_2O decomposition, the product yield is proportional to the change in logarithmic value of the conductivity. Based on

this assumption, the following equation is proposed:

$$P_{O_2} = k_4 \left\{ \left(\mu_p Na + \mu \frac{K_o}{nNa} \right) \Big/ \left[\mu_p \frac{K_o}{\frac{K_o}{Na} - k_G P_{N_2O} - \frac{\theta k_e P_{N_2O}}{k_f + k_g - k_h \theta}} \right. \right.$$

$$\left. \left. + \mu_n \left(\frac{K_o}{Na} - k_G P_{N_2O} - \frac{\theta k_e P_{N_2O}}{k_f + k_g - k_h \theta} \right) \right] \right\}^{k_5}$$

where P is partial pressure, μ is mobility, Na is concentration of acceptor atoms in the solid, K_o and the k's are constants, and θ is the fraction of the admolecules ionized.

This equation relates partial pressures with solid-state properties of the catalyst.

The only organic semiconductors studied to-date are the intrinsic ones. The usual terms in solid-state physics are applicable to these catalysts.

In long-chain polymers, the internal energy and the excitation energy for π electrons decrease with increase in polymer chain length.

The electron transport theory of catalysis would be equally applicable to organic semiconductors; however, organic catalysts are composed of molecular polymer chains. An alternating external electric field would be helpful to a reaction with an organic catalyst, and this subject was considered along with the type of sophisticated experimental equipment available for measuring the solid-state and surface properties of a catalyst during reaction.

F. Decomposition of Nitrous Oxide Catalyzed by Nickel Oxide

Experimental tests were conducted in a reactor that approximated an ideal back-mix reactor. The minimum conversions of nitrous oxide were twenty per cent. The reactor was operated at atmospheric pressure over a temperature range of 300 to 400°C. The input to the reactor was pure nitrous oxide at flows from 50 to 130 cc/min at 0.82 atm. and 24°C. The analysis of

the product stream was performed using a thermistor-type thermal conductivity cell.

The rate of decomposition of nitrous oxide was found to be highly dependent on the amount of oxygen adsorbed on the surface. In the first eight hours of a run, the rate was correlated in the form $r = kP_{N_2O}/(1 + KP_{O_2})$. This rate corresponds to the adsorption of oxygen being the rate controlling step. After ten hours of operating at steady conditions, the data were correlated using the form $r = kP_{N_2O}$. A first-order rate law applies if the catalyst surface is sparsely covered with oxygen. For nickel oxide, saturation coverage for adsorbed oxygen is one per cent of the total surface area.

G. Pyrolyzed Polyacrylonitrile as a Catalyst for the Nitric Oxide Reaction

Studies were conducted to determine if pyrolyzed polyacrylonitrile (PAN) would serve as a catalyst for the decomposition of nitric oxide. Investigations of the reduction reaction were carried out with PAN pyrolyzed at various temperatures between 400°C and 900°C under a nitrogen atmosphere, and also with a preliminary pyrolysis step in air up to 230°C.

The results indicated that PAN is not a catalyst for the decomposition of NO but enters into the reaction sequence. This conclusion stems from an analysis of the reaction products by gas chromatography which indicated the presence of both CO and CO_2 with CO_2 predominating. In all cases the inlet stream consisted of NO and helium only. Several possible mechanisms are consistent with these results. For example,

$$NO + \text{active site} \rightarrow N^* + O^*$$
$$2N^* \rightarrow N_2$$
$$O^* + C \rightarrow CO^* \rightarrow CO$$
$$CO^* + O^* \rightarrow CO_2^* \rightarrow CO_2$$

or

$$NO + C \rightarrow NOC \rightarrow N + CO$$
$$2N \rightarrow N_2$$
$$N + NO \rightarrow N_2O$$
$$CO + N_2O \rightarrow CO_2 + N_2$$
$$C + N_2O \rightarrow N_2 + CO$$
$$CO + NO \rightarrow N + CO_2$$

Subsequent investigation of the decomposition of NO over active carbon revealed that the reaction products again consisted of N_2, CO, and CO_2. However, the activated carbon on a per weight basis did not prove to be as effective in reducing NO as any of the PANs investigated. Furthermore, in this case N_2O was detected as one of the products produced. It was also observed that activated carbon rapidly loses its ability to reduce NO, while PAN appears to maintain the same level of ability for a prolonged period of time. This clearly indicates that the structure of PAN and not just the presence of carbon atoms alone is a factor in determining the effectiveness of PAN in reducing NO.

PAN pyrolyzed at 400°C was the most effective of all the PANs tried in reducing NO. Further, the PAN which had a preliminary pyrolysis step in air was more effective than the PAN pyrolyzed in a nitrogen atmosphere exclusively for each pyrolysis temperature investigated. This is most probably due to differences in the chemical structure of PAN under different pyrolysis conditions.

H. Measurement of the Electrical Conductivity of Pyrolyzed Polyacrylonitrile

A study was made of the electrical conductivity of pyrolyzed polyacrylonitrile in a helium atmosphere at atmospheric pressure. Studies were made in a temperature range from 150°C to 230°C, in which range helium was assumed to be unadsorbed. Electrical conductivity of pyrolyzed polyacrylonitrile was also measured in atmospheres of nitrogen, isobutylene, and water. In these studies, nitrogen was used as the diluting gas and was assumed to be unadsorbed.

The electrical conductivity measurements in helium were correlated by the equation $\sigma = \sigma_0 \exp(-E/2kT)$ with $E = 1.48$ ev. and $\sigma_0 = 0.135$ $(\text{Ohm-centimeter})^{-1}$. Similar results were obtained for conductivity effects in a nitrogen atmosphere.

There was a definite change in the electrical conductivity of pyrolyzed polyacrylonitrile when water or isobutylene were included in the surrounding atmosphere. In general, the conductivity first increased with time and then decreased steadily as the pyrolyzed polyacrylonitrile was exposed to the vapors. There appeared also to be an effect on the conductivity based on the rate at which the vapor was passed across the

polyacrylonitrile surface. The change in conductivity in the presence of the vapors appeared to be an irreversible one, and it was very difficult to obtain reproducible experimental results.

IV. Personnel

An important goal of university research is the training of future scientists. This grant has supplied support and training for seven graduate students in chemical engineering at the University of Colorado (Dr. Michael B. Cutlip, Dr. Charles A. Leech, III, Mr. Eugene E. Sterbis, Mr. David Y. Yuen, Mr. Thomas Gilman, Mr. Lynn Rice, and Mr. John Sanderson). One undergraduate research assistant (Mr. Wayne Vanderpool) and two post-doctorates (Dr. John Shen and Dr. David G. Retzloff) also received support and training from the grant. A number of other students in chemical engineering at the University of Colorado also benefited from this grant by seminars and other contacts with the persons who were directly involved in the research program.

V. Publications

Four M.S. degrees and two Ph.D. degrees have been awarded to graduate students benefiting from this research program. A list of publications resulting from this research is presented in the following:

1. "Electron Transport and Solid-State Characteristics of Catalysts," David Y. Yuen, 1966, M.S. thesis, University of Colorado.
2. "Decomposition of Nitrous Oxide Catalyzed by Nickel Oxide," Eugene E. Sterbis, 1966, M.S. thesis, University of Colorado.
3. "Highly Conjugated Organic Polymers as Catalysts for the Dehydration of Tertiary Butyl Alcohol and the Decomposition of Nitrous Oxide," Thomas C. Gilman, 1968, M.S. thesis, University of Colorado.
4. "Kinetic Studies of the Nitrous Oxide Decomposition Reaction Catalyzed by Nickel Oxide," Charles A. Leech, III, 1968, M.S. thesis, University of Colorado.
5. "Kinetic Studies on the Catalytic Gas Phase Dehydration of Tertiary Butyl Alcohol over Pyrolyzed Polyacrylonitrile," Michael B. Cutlip, 1968, Ph.D. thesis, University of Colorado.

6. "Kinetic Studies of the N_2O-CO Reaction Catalyzed by Chromium-Promoted Iron Oxide," Charles A. Leech, III, 1970, Ph.D. thesis, University of Colorado.

7. "Heterogeneous Catalysis over an Organic Semiconducting Polymer made from Polyacrylonitrile," M. S. Peters and M. B. Cutlip, Chem. Eng. Prog. Symposium Series, 64, No. 89, 1 (1968).

8. "The Role, Sources, and Control of Nitrogen Oxides in Air Pollution," M. S. Peters, Chem. Ing. Technik, 41, Nr. 10, Mai, 593 (1969).

9. "Engineering Action Needed for Pure Air," M. S. Peters, Chem. Eng. Prog., 64, No. 12, 29 (1968).

10. "Summary of Present Knowledge of the Chemistry of Air Pollution," M. S. Peters, Paper 12A, Session 12, 62nd Annual AIChE Meeting, Washington, D.C., November 18, 1969. Paper accepted for publication in AIChE Symposium Series.

11. "Literature Survey of Air Pollution Abatement Reactions with Special Emphasis on Rare Metal and Rare Earth Catalysts," Lynn H. Rice, University of Colorado, August 18, 1969.

12. "Kinetic Studies of the N_2O-CO Reaction Catalyzed by Chromium-Promoted Iron Oxide," C. A. Leech, III, and M. S. Peters, paper in preparation.

VI. Technical Talks

A list of technical talks resulting from this research project is presented in the following:

"Explanation of Catalytic Activity of Organic Semiconductors by Solid-State Principles and Electron Transport" by David Y. Yuen and Max S. Peters. Paper presented at Free Forum of Annual AIChE Meeting in Philadelphia, Pa., December 8, 1965.

"Summary of Present Knowledge of the Chemistry of Air Pollution," M. S. Peters, 62nd Annual AIChE Meeting, Washington, D.C., November 18, 1969.

"Role, Sources, and Control of Nitrogen Oxides in Air Pollution" - This talk with different degrees of technical depth was presented to approximately 40 different technical groups during the past three years. Locations and dates of some of the more technical presentations are given

in the following:

American Institute of Chemical Engineers, Local Section Meetings at

St. Louis, Missouri (April 14, 1967)
Pittsburgh, Pennsylvania (Oct. 4, 1967)
New York City (Oct. 16, 1967)
Syracuse, N. Y. (Oct. 17, 1967)
Schenectady, N. Y. (Oct. 18, 1967)
Pampa, Texas (Dec. 14, 1967)
Detroit, Michigan (Jan. 10, 1968)
Salt Lake City, Utah (March 21, 1968)
Los Angeles, California (April 25, 1968)
Tucson, Arizona (May 2, 1968)
Kansas City (May 8, 1968)
Columbus, Ohio (Oct. 15, 1968)
State College, Pennsylvania (Nov. 7, 1968)
Cincinnati, Ohio (Dec. 9, 1968)
Denver, Colorado (Dec. 17, 1968)

Chevron Research Co., San Francisco, Calif. (April 21, 1967)
Gesellschaft fuer Verfahrens-Ingenieure, Stuttgart, Germany (Oct. 1, 1968)
Colorado School of Mines, Golden, Colorado (Dec. 5, 1969)
University of Pennsylvania, Philadelphia (April 27, 1970)
University of Michigan, Ann Arbor (Jan. 14, 1971)
Corning Glass Works, Corning, N.Y. (Feb. 22, 1971)